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Enhancement of spontaneous emission rate and reduction in amplified spontaneous emission threshold in electrodeposited three-dimensional ZnO photonic crystal

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ZnO photonic crystal (PC) with face-center-cube type structure is fabricated by electrodeposition using holographic lithographically made organic (SU-8) template. Photonic band gap effect (reflection peak and transmission dip in infrared spectral region) is clearly seen. Observation of strong enhancement and blueshift of the emission peak (from 383.8 to 378.8 nm), shortening of the exciton photoluminescence lifetime (from 88 to 34 ps), and reduction in amplified spontaneous emission threshold of ZnO PC compared to that of the reference nonstructured electrodeposited ZnO showed clear evidence of PC structure affecting the ZnO exciton emission. © 2010 American Institute of Physics. [doi:10.1063/1.3499274]

Due to their promising potential for miniaturization and integration of optical devices, photonic crystals (PCs) have been extensively studied since the first proposal in 1987.¹ A number of techniques such as self-assembly, multiphoton polymerization, and holographic lithography (HL) have been used to make PCs.^{2–4} However, to achieve a full photonic band gap, it is necessary to use a high refractive index material. This is typically achieved by infiltration of a high refractive index material in a PC template.^{5,6} Infiltration can be accomplished by different methods, such as chemical vapor deposition (CVD) and atomic layer deposition (ALD).^{2,5,6} However, both of these methods are conformal coating approaches, which will result in an incomplete filling of the template due to pinch-off problem,^{7,8} which can lead to the loss of photonic band gap.⁸ Unlike conformal coating processes such as CVD or ALD, inexpensive solution-based techniques such as electrodeposition^{9,10} and electrophoretic deposition⁸ allow almost complete filling of the template.

Among various materials for infiltration, ZnO appears to be a very interesting one because of its relative high refractive index ($n \sim 2.0$) and its remarkable properties as a semiconductor and transparency in the visible range of the spectra.¹¹ Recently, high-quality ZnO inverted opals grown by different methods^{5,6,12} have been reported. However, the templates used in these previous works were fabricated by self-assembly method, which can only be fabricated face-center-cube (fcc) and close-packed hexagonal lattice. Here we demonstrate the use of HL to prepare ZnO PCs. HL is one of the most promising techniques for mass production of large area, defect free one-, two-, and three-dimensional PC structures.¹³ It was proven that umbrellalike multibeam interference could fabricate all bravais lattices,¹⁴ and various other ordered structures. Recently, we have developed a HL

technique using a single-beam and a refracting prism to split and combine the beams to make the desired interference pattern.^{13,15} This single-beam and single-refracting prism HL technique is very simple and stable compared to conventional multibeam and multielements setup.

The templates were fabricated by single beam HL using photoresist (SU-8) deposited on indium tin oxide coated glass substrate, with the details of the procedure and schematic illustration of the setup given in Ref. 13. Figure 1(a) shows the scanning electron microscopy (SEM) image of the organic template. The inset is the cross section of the template. A high quality, defect free fcc-type structure was clearly seen in these SEM images. Figure 1(b) is the simu-

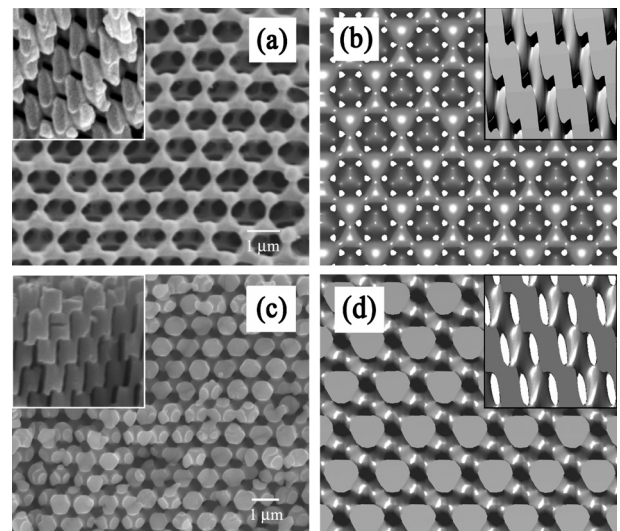


FIG. 1. (a) The SEM images of PC template. The figure inset is the cross section of the sample. (b) The computer simulation of (a). (c) The close-up SEM image of the ZnO inverse PCs. The inset is the cross section of the sample. (d) shows the computer simulation of (c).

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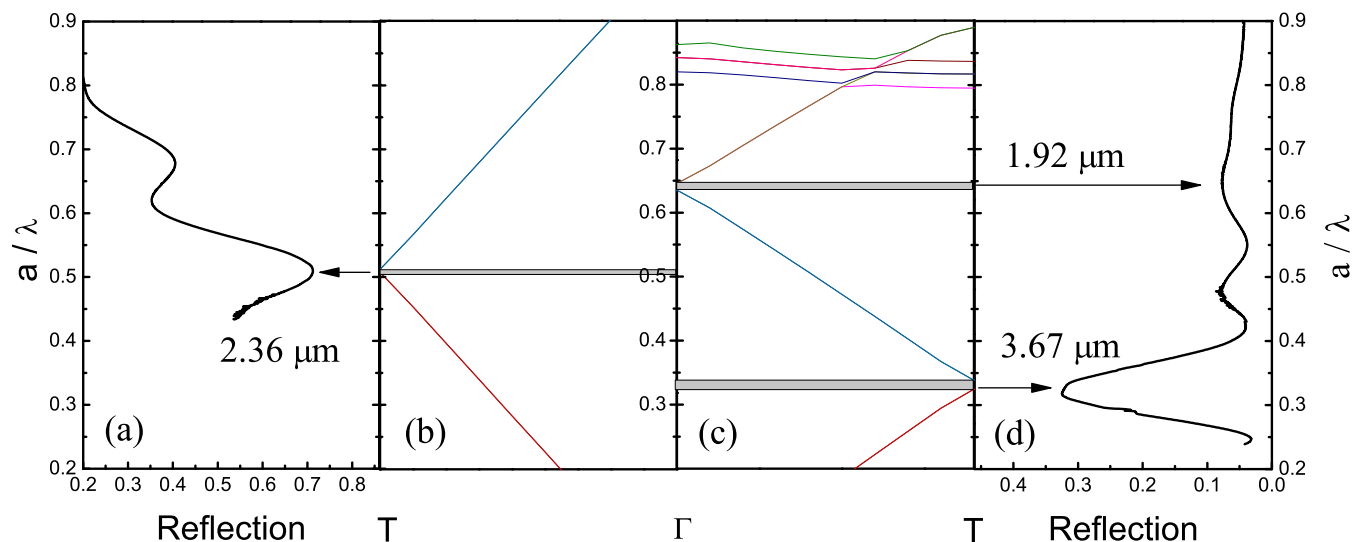


FIG. 2. (Color online) (a) Optical intensity reflection spectrum of the fcc-type photoresist template in Fig. 1(a), showing one pronounced peaks around $2.36 \mu\text{m}$. (b) Corresponding band-structure calculation along the measured direction (Γ -T). (c) Corresponding band-structure calculation of the ZnO inverse PC in Fig. 2(a). The gray shaded area corresponds to the band gap at the measured direction. (d) Optical intensity reflection spectrum of the ZnO inverse PC in Fig. 2(a), showing one pronounced peaks around $3.67 \mu\text{m}$ and two shoulders at 2.60 and $1.92 \mu\text{m}$.

lation of the interference pattern which shows good agreement between the experimental result and simulation.

ZnO was infiltrated into the HL made organic template using electrodeposition technique. After electrodeposition, the samples were rinsed by deionised water and ethanol respectively, and then annealed at 500°C in air for 30 min. to remove the polymer template. Large area and high quality ZnO microstructure with fcc-type lattice was obtained. The uniform area is about 10 mm^2 . Figure 1(c) shows the close-up of the ZnO inverse structure. The inset is the cross section of the sample. Complete filling of the SU-8 template pore network by ZnO without any discontinuity is clearly seen. The simulation of the interference pattern is shown in the Fig. 1(d). All the SEM images are in good agreement with the simulation.

Figures 2(a) and 2(d) show the reflection spectra of the SU-8 template and ZnO inverse PC, respectively. The SU-8 template's reflection peak is around $2.36 \mu\text{m}$, whereas ZnO inverse sample's major reflection peak is around $3.67 \mu\text{m}$. These two reflection peaks are in good agreement with the two pronounced dips in transmission. The reflection peak of the ZnO inverse sample is redshifted to that of the SU-8 template since the refractive index of the ZnO is higher than that of the SU-8. We also calculated the band structure by using the plane wave expansion method with the parameters deduced from Figs. 1(a) and 1(c). In the case of Fig. 1(a), the parameters are as follows: the lattice spacing is $1.21 \mu\text{m}$ and the filling factor of the SU8 is 35.35%. In the case of Fig. 1(c), the parameters are as follows: the lattice spacing is $1.23 \mu\text{m}$ and the filling factor of the ZnO is 67.50% (the difference of the lattice spacing is due to the annealing of ZnO). The refractive index for SU-8 and ZnO were chosen to be 1.6 and 2.0, respectively. The band structures of SU-8 template and ZnO inverse samples are shown in the Figs. 2(b) and 2(c), respectively.

From the measured and calculated results shown in Fig. 2, it can be observed that the position of the major peak in reflection corresponds well with the first partial stop band (outlined by the gray shaded square) expected from the band structure calculation for the measured direction. Where, the

Γ -T is $[1\ 1\ 1]$ direction of the fabricated fcc-type PCs, which is the measured direction. There are two shoulders in the reflection spectra of the ZnO infiltration structure. The first one at $2.60 \mu\text{m}$ is due to the Fabry-Perot effect of the thin film and the second one at $1.92 \mu\text{m}$ is good corresponding to the second partial stop band [outlined by the gray shaded square in Fig. 2(c)].

Figure 3(a) shows the photoluminescence (PL) spectra of the ZnO PC and the bulklike porous ZnO fabricated on the same substrate and at the same time but outside the area with PC structure, which we will refer to as the reference material. The PL peak of the ZnO PC blueshifted to about 378.8 nm , which is corresponding to the transmission dip of this sample. The transmission of the reference ZnO showing typical transmission step at band edge for bulk ZnO. Furthermore, band edge exciton is five times more intense for ZnO PC compared to nonstructured PC under the same cw laser (He-Cd laser at 325 nm) excitation condition [see Fig. 3(b) inset]. This result clearly shows the PC structure strongly enhanced the exciton UV emission in ZnO. Furthermore, peak intensity ratio of band edge exciton peak to the impurity/defect emission peak (580 nm) is about 1:1 for the ZnO PC, whereas this ratio drops to 1:6 for the nonstructured ZnO region. We also observed a difference in the exciton PL lifetime (τ) obtained from the time-resolved PL measurements (by fitting the curves to a single exponential decay model). As shown in Fig. 3(b), ZnO PC exhibited τ of $\sim 34 \text{ ps}$, which is much shorter than that of the reference ZnO (about 88 ps). Reduction in the ZnO PC PL lifetime to 38.6% of that of the reference ZnO indicates that the partial photonic band gap of the structure has enhanced the spontaneous emission rate of ZnO. It is known that a photon inhibition takes place if an electronic transition wavelength overlaps with the photonic band gap, and the transition is limited by the photon density of state (DOS). In this situation, the transition probability p varies as the photon DOS, $p = 1/\tau \propto \text{DOS}$. So, the decrease in the lifetime is likely due to the increase in the photon DOS of the photon at the higher order photonic band edge. Recently, Cao and co-workers¹⁶ have

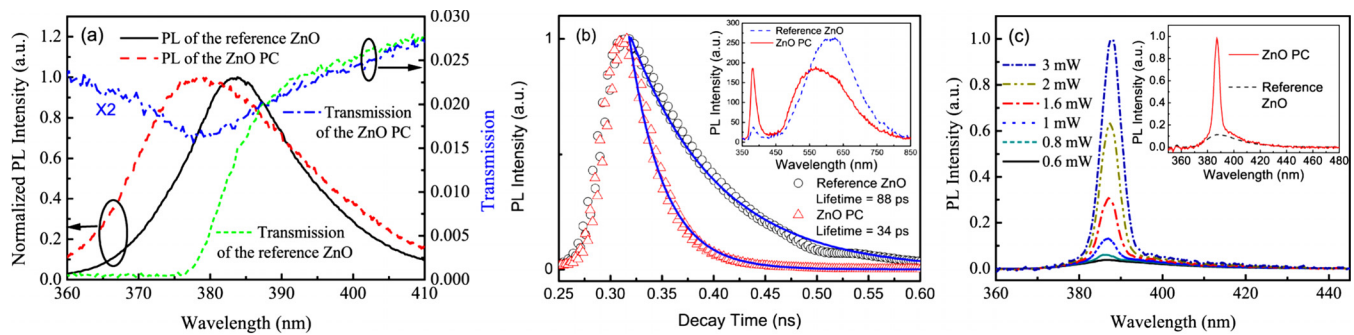


FIG. 3. (Color online) (a) PL and transmission spectra of the ZnO PC and the reference ZnO. (b) Time-resolved measurement of the reference ZnO (black circle) and the ZnO with PC structure (red triangle). The blue solid lines are single exponential fitting curve of the data. The figure inset shows the comparison of the exciton emission intensity of the reference ZnO (red solid curve) and the ZnO with PC structure (blue dashed curve) under the same excitation condition. (c) Emission spectrum as a function of excitation power for the ZnO PC. The figure inset shows the ASE/PL spectra for ZnO PC and nonstructured ZnO at the same excitation intensity of 6.4 mJ/cm².

indeed shown that spontaneous emission is strongly modified by DOS for ZnO inverse opal structure. The enhanced spontaneous emission rate also manifested in significantly reduced threshold for the amplified spontaneous emission (ASE) in the PC ZnO compared to reference material. Figure 3(c) displays the emission spectra of the PC ZnO as a function of excitation intensity. A sharp emission peak appears on top of the broad spontaneous emission band at an excitation threshold of ~ 4 mJ/cm² (corresponded to ~ 1 mW excitation power). A nonlinear increase in the emission intensity as a function of pumping energy and a corresponding reduction in emission spectral width (full width at half maximum) above the ASE threshold is also clearly seen. The inset of Fig. 3(c) shows the emission spectra of ZnO with and without the PC structure at the same excitation intensity, sharp ASE peak is clearly seen for the ZnO with fcc-type structure, while nonstructured reference ZnO only shows the broad spontaneous emission band. It is well known that ZnO in various forms can easily produce lasing effect under moderate optical excitation intensity.^{17–19} Indeed, both of the electrodeposited ZnO PC and nonstructured ZnO can produce ASE but the ASE threshold for the PC ZnO is ~ 4 mJ/cm² which is about three times smaller than the nonstructured ZnO, in agreement with previous report on the reduction in lasing threshold in ZnO PC.¹²

To summarize, the infiltration of ZnO using electrodeposition into the PC polymer templates prepared by HL technique has been achieved. Complete filling of the narrow pores without any discontinuity is seen. Clear enhancement of spontaneous emission and lowering of the ASE threshold is seen for the ZnO with PC structure.

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